Mintek's Integrated cloSURE™ Technology for Treatment of Acid Mine Drainage

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Abstract

Mintek has developed cloSURE™ for treatment of AMD. The process consists of two stages, biological sulfate reduction followed by oxidation for sulfide removal and biosulphur production. The process was demonstrated at laboratory scale and achieved sulfate reduction rates of 196 $g/m^3/d$ with 87% sulfate removal, and up to 98% sulphide removal. The pH level increased to 7.5 and metals were found to be within South African target water quality limits for irrigation. The results of the research show that cloSURE™ is a potential solution for sustainable treatment of point sources of AMD.

Keywords: Biological Sulfate Reduction, Mine Water Treatment, Acid Mine Drainage, Water Re-use

Introduction

The legacy of acid mine drainage (AMD) in South Africa has caused widespread contamination of river catchments. The AMD is typically characterised by high sulfate concentrations, in excess of 3 g/L, with relatively low concentrations of metals. Currently there is no sustainable solution for point sources of AMD discharge in remote locations in South Africa.

Mintek has developed cloSURE™, a technology which employs biological processes to treat mine impacted water. The aim is to produce water that is fit for re-use in irrigated agriculture. cloSURE™ is suitable for small point sources in remote locations that lack services and infrastructure, such as legacy mines and mines after closure. The process consists of two stages, namely a biological sulfate reduction (BSR) step followed by an oxidation step for sulfide removal and biosulphur production.

Stage 1 employs biological sulfate reduction to remove sulfate, increase alkalinity and pH, and remove metals. Biological sulfate reduction employs anaerobic, sulfate reducing bacteria (SRB) which are present in natural environments such as the sediment of lakes and wetlands, cattle rumen and subsequent manure. SRB use sulfate as the terminal electron acceptor for cellular respiration, and consume simple organic substrates such as lactate and acetate for energy (Hansen 1993). These organic substrates are converted to bicarbonates which raise the alkalinity and pH of the treated water. The biological reduction of sulfate produces sulfide that bind to the metals in solution to form metal sulfides, which are stable at neutral pH, reducing metal concentrations in the effluent to trace amounts (van Hille *et al*. 2019). There is also potential for selective recovery of the retained metal sulfides.

The primary reactions are as follows:

$$2CH_2O(aq) + SO_4^{2-} + H+ \rightarrow H_2S+2HCO_{3^-} \quad [1]$$

$$H_2S + Me^{2+} \rightarrow MeS + 2H^+ \quad [2]$$

Reduction of sulfate results in the production of sulfide which can be corrosive to irrigation equipment and may pose a safety risk to plant operators. In the second stage of the process, the focus is on the biological removal of sulfide and residual metals, and the recovery of biosulphur, in order to produce treated water that is fit for use in irrigated agriculture. Sulfide oxidising bacteria are found in aquatic systems in floating bacterial mats, and oxidise sulfide to sulphur and sulfate with increasing concentrations of oxygen. Sulfide is partially oxidised to sulphur under conditions where the stoichiometric ratio of sulfide to oxygen is greater than 2:1 (Buisman *et al.* 1990; van Hille and Mooruth 2011):

$$2HS^{-} + O_2 \rightarrow 2S^0 + 2OH^{-} \quad [3]$$

When more oxygen is available, sulfide oxidisers readily produce sulfate:

$$2HS^{-} + 4O_2 \rightarrow 2\ SO_4^{2-} + 2H^{+} \quad [4]$$

For the purposes of cloSURE™'s stage 2 treatment, partial oxidation of sulfide to sulphur is preferred to minimise the production of sulfate, which would nullify the effects of the biological sulfate reduction treatment step. Sulphur oxidisers are cultivated in a floating biofilm in an oxidation tank. This biofilm prevents escape of any hydrogen sulfide to the atmosphere and minimises diffusion of oxygen into the tank, ensuring maximum sulfide concentrations and minimum oxygen concentrations.

Development of Stage 1 culminated in an 18 month pilot study at a mine site (Neale *et al.* 2018), treating 250 L/d, and removing 95% of the sulfate from the mine water. At the time of piloting Stage 1, the Stage 2 concept was being developed in the laboratory.

The cloSURE™ process produces significantly less solid waste, with decreased toxicity and increased stability, compared to conventional chemical precipitation methods. It requires relatively low capital costs, and operating costs can be greatly reduced when using inexpensive carbon sources and/or passive or semi-passive treatment designs.

The aim of this study was to demonstrate the integrated treatment process at small scale and assess the quality of the treated water as fit-for-use. The objectives were to:

1. Run an integrated cloSURE™ treatment process at laboratory scale and obtain sufficient data assess the quality of the water.
2. Assess the suitability of the water for irrigation purposes against the irriga tion target water quality guidelines (DWAF 1996)
3. Analyse the components of the biofilm formed.

Method

cloSURE™ Process Setup

An integrated process was set up at Mintek, to treat 5.2 L of AMD per day and is shown in Figure 1:

1. Stage 1: Biological sulfate reduction column
2. Stage 2: Sulfide oxidation tank

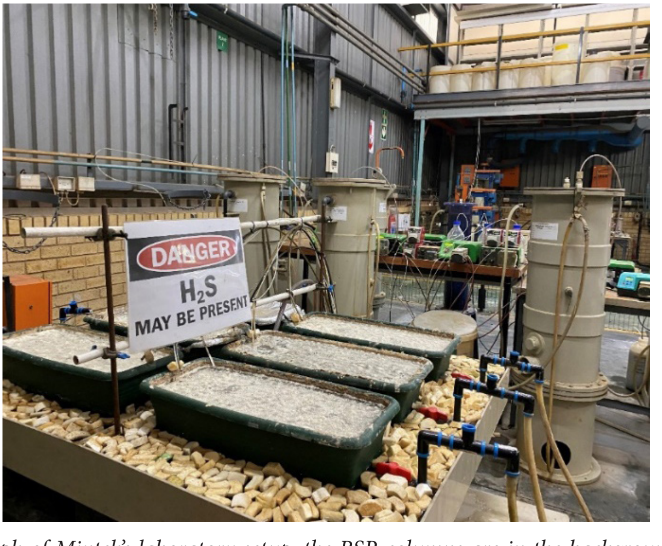

Figure 1 *Photograph of Mintek's laboratory setup, the BSR columns are in the background and the sulfide oxidation tanks are in the foreground.*

The Stage 1 BSR column consisted of a packed bed of woodchips, and had a working volume of 50 L. The column was inoculated with an effluent sample from Mintek's pilot plant, containing a representative consortium of microbes including SRB. The temperature was maintained at 35 °C. Raw mine water was obtained from a coal mine site in Mpumalanga Province, South Africa, with sulfate concentrations between 2.5 g/L and 4.0 g/L, and a pH level of 3. Table 1 gives the parameters of the neutralised feed water. The water was neutralised with lime to pH 6. The carbon source was cow manure, which was removed and replaced with fresh manure at weekly intervals. The column was continuously operated with a hydraulic retention time (HRT) of 10 d and a flow rate of 5.2 L/d.

The Stage 2 sulfide oxidation tank had a horizontal flow configuration and a working volume of 14 L. The tank consisted of a packed bed of polypropylene biofilter material, one third the depth of the tank, the surface of the water was inoculated with dried biofilm from prior Mintek laboratory work, to encourage the development of a floating sulphur biofilm. Nutrients were added the form of ammonium sulfate, di-potassium hydrogen phosphate and glycerol. The tank was continuously operated with a flow rate of 1.4 L/day to achieve a HRT of 10 days.

Target Water Quality Limits for Irrigation

The South African Water Quality Guidelines for Irrigation Water Use (DWAF 1996) is a specification of the required water qualities for various irrigation uses. The guideline provides limits in order to assess the fitness of the water to be used for irrigation activities, primarily crop production. It gives three concentrations ranges for water qualities:

1. Target Water Quality Range (TWQR) which is considered a satisfactory concentration for continuous application with no impact on soil or crop yield.
2. The maximum acceptable concentration for fine textured neutral to alkaline soils
3. Acceptable for irrigation only over the short term on a site-specific basis

This study compared metals concentrations to the more stringent TWQR only.

Analyses

Both the BSR column and sulfide oxidation tank were sampled twice weekly for pH, redox potential, temperature, electrical conductivity, and sulfide and sulfate concentrations

Redox potential and pH were measured directly using pH and ORP electrodes (Knick Partavo 904(X) meter with Metrohm pH probe, 6.0220.100 Hamilton Liq Glass ORP probe). Electrical conductivity (EC) was determined using an EC probe (WTW Cond 330 meter and WTW TetraCon325 probe).

Sulfate was determined using Merck sulfate cell tests (100-1000 mg/L and 0.5-50 mg/L) and Prove 300 spectroquant. Sulfide was determined by the potentiometric method, using a Metrohm Tiamo autotitrator and AgS titrode, titrated against silver nitrate. Sulfide samples were preserved with NaOH and analysed immediately.

Once stable results were obtained in both stages, water samples were collected and sent for metals analysis at Waterlab. Pretoria. Metals samples were filtered and preserved with HNO_3, and metals were analysed with ICP-MS.

The biofilm was harvested every 14 days. A sample was dried and weighed, and analysed at Mintek using ICP, Leco sulphur analysis and X-Ray Diffraction (XRD) Analysis

Table 1 *Average parameters for the neutralised feed water over the study period.*

Parameter	Average Value
Sulphate Concentration (mg/L)	2 775
Sulphate Loading Rate (g/m3/d)	237
Flow Rate (L/d)	5.2
pH	6.5
Substrate: Cow Manure (kg/wk)	1.5

Results

Sulfate and Sulfide Removal

The cloSURE™ treatment vessels had been running for approximately one year, but had to be stopped for four month during the Covid-19 Lockdown. Day 0 in this paper refers to the restart date after the lockdown period. After startup, the column had elevated levels of sulfate, which decreased from Day 35. Between Day 35 and Day 80, an average volumetric sulfate reduction rate of 173 g/m³/d (1.48 mol/m³/d) and 57% sulfate removal was attained. From Day 90 the volumetric sulfate reduction rate increased and stabilised at an average of 196 g/m³/d (2.05 mol/m³/d), with 87% sulfate removal. Sulfate concentrations and salfate reduction rates over the study period are shown in Figure 2.

Typical values for sulfate reduction in passive treatment processes range between 28 g/m³/d (0.3 mol/m³/d) and 76 g/m³/d (0.8 mol/m³/d) (Gusek 1998; Pulles *et al.* 2016). While the laboratory cloSURE™ process is not strictly a passive process due to the addition of substrate on a regular basis, the sulfate reduction rates achieved were much higher than expected for a process fed with a complex substrate, and indicate promising potential as a treatment technology.

In Stage 2, the sulfate initially increased as the sulfide was oxidised to sulfate. Once the biofilm was established, sulfate was no longer produced in the oxidation stage from Day 35, indicating that sulfide removed was converted to sulphur in the biofilm. The sulfide graph in Figure 3 illustrates that from Day 80, increased sulfate reduction rates produced high concentrations of sulfide in the Stage 1 treated water. Once the biofilm had established in Stage 2, partial sulfide oxidation occurred and sulfide concentrations in the treated water remained low, with 78–98% of the sulfide removed.

pH levels increased through the process, with a pH of 7.5 from Day 80, during stable operation, indicated in Figure 3. The pH remained constant irrespective of the fluctuating feed pH, indicating alkalinity production and a stable Stage 1 (BSR) reactor.

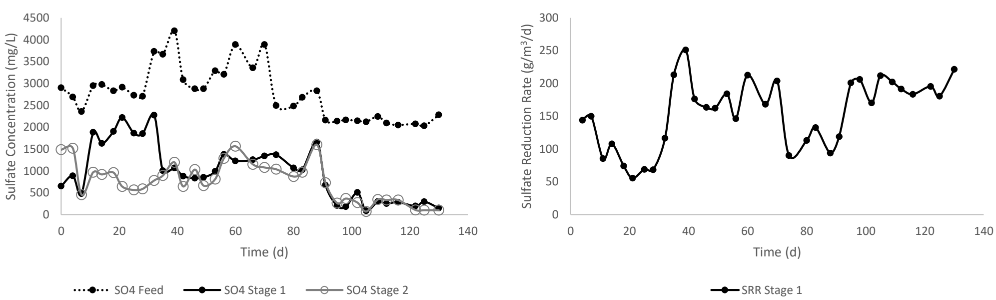

Figure 2 *Sulfate concentrations (left) in the neutralised feed and each Stage of the process, and volumetric sulfate reduction rates (SRR) (left) for Stage 1.*

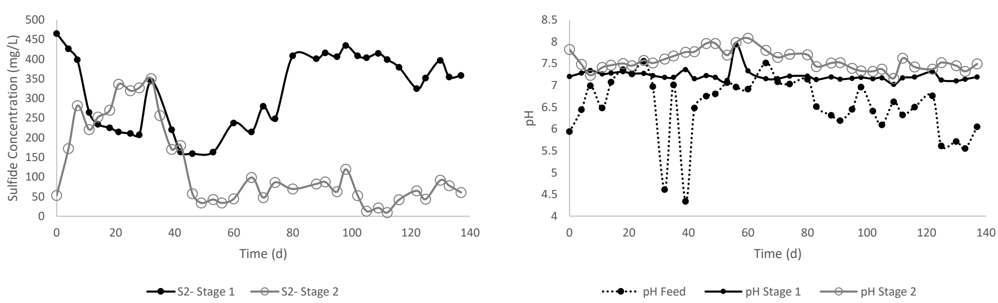

Figure 3 *Sulfide concentrations (left) and pH (right) of the neutralised feed and each Stage of the process.*

Table 2 *Metals concentrations in the neutralised feed and each Stage of the process.*

	AMD Feed	Neutralised Feed	Stage 1	Stage 2	TWQR
			mg/L		
Cl	13	12	-	-	100
F	<0.2	<0.2	<0.2	<0.2	2
Na	65	65	172	330	-
Ca	516	622	367	117	-
Mg	136	131	283	344	-
Al	111	2.59	0.525	0.551	5
As	0.001	<0.001	0.001	<0.001	0.1
Be	0.053	0.001	<0.001	<0.001	0.1
B	0.729	0.587	0.531	0.712	0.5
Cd	<0.001	<0.001	<0.001	<0.001	100
Cr^{6+}	0.06	<0.01	<0.01	<0.01	0.1
Co	0.015	0.011	<0.001	<0.001	0.05
Cu	0.05	0.034	0.034	0.029	0.2
Fe	43	0.92	0.208	0.238	5
Pb	0.0008	0.002	0.002	0.002	0.2
Li	0.287	0.26	0.132	0.267	2.5
Mn	1.4	1.18	0.199	0.015	0.02
Mo	<0.001	<0.001	<0.001	<0.001	0.01
Ni	0.543	0.257	0.092	0.105	0.2
Se	<0.001	<0.001	<0.001	<0.001	0.02
V	<0.025	0.049	<0.025	<0.025	0.1
Zn	2.1	0.741	0.071	0.499	1

Biofilm

Sulphur results indicated that 24% of the biofilm consisted of total sulphur and 20% elemental sulphur by mass. The biofilm yield was 234 g/m^2 for a single harvest. Research at the University of Cape Town indicates that hydraulic retention times of 2-3 days increase sulphur accumulation in the film up to 90% by mass (Personal Communication, Rob van Hille, 2019). Long retention times of more than 4 days yielded 25-40% sulphur by mass in the biofilm with a large organic and inorganic component. This suggests that higher yields can be achieved with optimisation of residence time in the integrated treatment system.

Results from ICP analysis (and confirmed by XRD) of the biofilm indicate the presence of magnesium (7.11%) and calcium (2.91%), as well as small amounts of manganese (0.11%) and iron (0.05%). XRD analysis indicated the magnesium is present in the form of struvite ($(NH_4)MgPO_4 \bullet 6(H_2O)$), and makes up 74% of the biofilm by mass. Calcium, iron and manganese are present in much lower levels in the forms of bixbyite ($(Mn,Fe)_2O_3$), graftonite ($(Fe,Mn,Ca)_3(PO_4)_2$) and ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$).

It is likely that the presence of magnesium phosphate compounds in the biofilm is also due to the high quantities of nutrients delivered to the Stage 2 system. Optimisation of nutrients and residence times may minimise the presence of inorganic compounds. There is potential for the oxidation stage to produce enough biofilm to be harvested and used as a valuable biosulphur fertiliser product, offsetting some of the treatment cost.

Target Water Quality Ranges

Table 2 gives the concentration of metals in the mine water, the neutralised mine water feed and the treated water. The TWQR (DWAF 1996) for each compound is given.

The parameters that exceed the TWQR are shaded in Table 1. These results confirm that the mine water consists of low concentrations of metals, and the majority of these fall within the TWQR without treatment. Aluminium, boron, iron, manganese, nickel and zinc are the exceptions. After neutralisation with lime, the concentrations of metals decrease to varying extents, but boron, manganese and nickel still exceed the TWQR. After treatment in both stages of the cloSURE™ process, all metals meet TWQR.

Other elements that remain in high concentrations in the effluent are magnesium, calcium and sodium. There are no individual water quality targets for these ions, however, they are used to calculate the sodium adsorption ration (SAR), which is a measure of the ratio of sodium to calcium and magnesium. The SAR for the treated water is 3.5 (calculated based on DWAF 1996). The impact of the SAR on soil quality is also dependent on the electrical conductivity, but generally the higher the ratio (>20), the greater the impact on soil permeability and infiltration (DWAF 1996).

Conclusion

With the number of coal mines due to close in the near future, cost effective technologies suited to remote locations are urgently required. The laboratory scale demonstration of the cloSURE™ process successfully removed sulfate in Stage 1, and removed sulphide in Stage 2, as well as increased the pH in the treated water. The biofilm in Stage 2 was able to successfully recover sulphur from the mine water, and based on its composition, could potentially be a value by-product from the water treatment process. The metals and SAR results show that the treated water is potentially fit for re-use in irrigated agriculture, however, this needs to be confirmed in irrigation trials and soil studies. The results of the research show that cloSURE™ is a potential solution for sustainable treatment of point sources of AMD, which will produce water that is fit for re-use in irrigated agriculture, in turn promoting economic hubs and food security in post-mining regions.

Future Work

The success of this study, led to a second piloting phase to test the integrated cloSURE™ process at scale. Funding has been granted to Mintek to demonstrate the process at scale at a mine site in Mpumalanga. Part of the scope of these projects is to evaluate the economics and logistical requirements for a field scale cloSURE™ process, as well as complete field irrigation trials using the treated water.

Acknowledgements

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